

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08J 3/05, 3/03, C08L 33/06, 39/08, C10L 1/10		A1	(11) International Publication Number: WO 98/51731 (43) International Publication Date: 19 November 1998 (19.11.98)
(21) International Application Number: PCT/EP97/02705		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 14 May 1997 (14.05.97)		Published <i>With international search report.</i>	
(71) Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).			
(72) Inventors: BRAAMS, Johannes, Franciscus, Hendrikus; Badhuisweg 3, NL-1031 CM Amsterdam (NL). REYNHOUT, Marinus, Johannes; Badhuisweg 3, NL-1031 CM Amsterdam (NL). IN 'T VEEN, Bernardus, Cornelis, Maria; Badhuisweg 3, NL-1031 CM Amsterdam (NL).			

(54) Title: POLYMER COMPOSITIONS**(57) Abstract**

Polymer compositions comprising a dispersion of at least one polymer A obtained by polymerisation of at least one olefinically unsaturated compound, which polymer contains aliphatic hydrocarbon side chains of at least 10 carbon atoms, in a continuous aqueous phase comprising a surfactant and at least one polymer B which comprises a thixotropic hydrophilic polymer, a process for the preparation of the compositions, and their use as pour point depressants.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

- 1 -

POLYMER COMPOSITIONS

This invention relates to polymer compositions, their preparation and their use as pour-point depressants.

Crude oils (crude mineral oils) and certain fuels (oils) derived therefrom, e.g. wax-containing fuel oils and diesel fuels, may contain considerable amounts of wax. This wax gradually separates out as such materials are cooled, and at sufficiently low temperatures these materials may solidify completely. The lowest temperature observed during a standard laboratory test (ASTM D.97) at which the waxy material still flows is called the "pour-point" of the material.

In order to overcome the problems arising from cooling of such materials in storage or in transport, whether in tankers or by pipeline, certain polymers have been developed which when added to such materials depress the pour-point of the material.

Such polymers are typically polymers obtained by polymerisation of at least one olefinically unsaturated compound, which polymers contain aliphatic hydrocarbon side chains of at least 10 carbon atoms, e.g C₁₀-30 aliphatic hydrocarbon side chains. Typically these polymers have molecular weights (M_n) in the range of 10,000 to 1,000,000.

Examples of such polymers are described in GB-A-1154966, GB-A-1161188, GB-A-1285087, GB-A-1410819, EP-A-0120512, EP-A-0236844 and US-A-4547202.

Whilst these polymers have proved to be very effective pour point depressants, and hence useful fluidity improvers, they are typically sold as concentrated solutions in solvents such as toluene or xylene, which solutions may themselves have relatively

- 2 -

high pour points. For dispersion in tanks of crude oil and fuel oil, this normally presents no significant problem. Examples of commercially available fluidity improvers include those available from the Royal Dutch/Shell Group of companies under the trade mark "SHELLSWIM - 5X", a 50%w solution of an alkyl acrylate polymer in xylene (having a pour point of 27°C), and under the trade mark "SHELLSWIM - 11T", a 50%w solution of an alkyl acrylate/vinyl pyridine copolymer in toluene (having a pour point of 18°C).

However, there are circumstances, for example where it may be desired to pass the fluidity improvers themselves along a pipeline in cold environments, e.g. in North Sea or Arctic areas, when it would be advantageous to have concentrated formulations of pour point depressants which would remain readily flowable at low ambient temperatures.

In EP-A-0448166, concentrated formulations have been disclosed containing an alkylacrylate polymer, a surfactant, a polyol and various amounts of water. It appears from said document that the best results (long term storage stability) are obtained when use is made of formulations containing a limited amount of water. Surprisingly, it has now been found that formulations which may contain high amounts of water constitute attractive pour point depressants, when they contain a thixotropic hydrophilic polymer.

According to the present invention there is provided a polymer composition comprising a dispersion of at least one polymer A obtained by polymerisation of at least one olefinically unsaturated compound, which polymer contains aliphatic hydrocarbon side chains of at least 10 carbon atoms, in a continuous aqueous phase comprising a surfactant and at least one polymer B which comprises a thixotropic hydrophilic polymer.

The polymer compositions according to the present

- 3 -

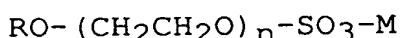
invention advantageously display a low viscosity under transport conditions and a long term storage stability.

Suitable polymers A are described in GB-A-1154966, GB-A-1161188, GB-A-1285087, EP-A-0120512, EP-A-0236844 and US-A-4547202. These polymers typically have molecular weights (M_n) in the range 10,000 to 1,000,000 and contain C₁₀-30 aliphatic hydrocarbon side chains. Preferably polymer A has a molecular weight (M_n) in the range 20,000 to 250,000, more preferably 25,000 to 10 100,000, e.g. 30,000 to 80,000.

Polymer A is preferably a homo- or copolymer of one or more (C₁₈-30 n-alkyl) acrylates or methacrylates, e.g. 1-docosyl acrylate (C₂₂), 1-octadecyl acrylate (C₁₈) and 1-eicosyl acrylate (C₂₀). Suitable copolymers are copolymers of one or more (C₁₈-30 n-alkyl) acrylates or methacrylates with a monoolefinically unsaturated compound having a nitrogen containing group, such as acrylonitrile, acrylamide, p-aminostyrene, N-vinylpyrrolidone or 4-vinylpyridine.

Most preferably polymer A is a polymer of one or more (C₁₈-26 n-alkyl) acrylates or a copolymer of one or more (C₁₈-26 n-alkyl) acrylates and 4-vinyl-pyridine).

Various non-ionic and ionic surfactants are suitable for incorporation in compositions according to the invention. Preferably the surfactant is selected from alcohol ethoxy sulphate surfactants and lignosulphonate surfactants. Such surfactants are typically alkali metal or ammonium salts. Alcohol ethoxy sulphate surfactants typically have the formula



where m is sodium or ammonium, R is C₁₂-18 alkyl and n is 2 or 3.

Compositions according to the invention suitably contain 0.1 to 20, preferably 1 to 15, more preferably

- 4 -

1 to 10 parts by weight of surfactant per 100 parts by weight of polymer A.

Polymer B comprises a thixotropic hydrophilic polymer. Solutions of such polymers are known to have
5 a high viscosity at a low shear rate and to have a low viscosity at a high shear rate. Suitable polymers B include for instance polysaccharides (e.g. Xanthan Gum) and partly hydrated polyacrylamides. These polymers typically have number average molecular weights (M_n) in
10 the range 1×10^5 to 1×10^7 , preferably in the range 5×10^5 to 5×10^6 .

Suitably, these polymers have a molecular weight distribution (M_w/M_n , whereby M_w is defined as the weight average molecular weight) in the range 1 to 5,
15 preferably 1 to 2, most preferably 1 to 1.5.

Polymer B is preferably a polysaccharide. Most preferably polymer B is Xanthan Gum.

Compositions according to the invention suitably contain 0.01 to 20, preferably 0.1 to 10, more
20 preferably 0.2 to 5, parts by weight of polymer B per 100 parts by weight of polymer A. These amounts include any minor amounts of solvents such as ethanol which may be present in the surfactant chosen for incorporation in the composition.

25 Other additives may be incorporated in minor amounts in the compositions of the invention such as anti-oxidants, anti-corrosion agents or metal deactivators.

Compositions according to the invention suitably contain more than 20, preferably more than 50, more
30 preferably more than 80, parts by weight of water per 100 parts by weight of polymer A.

The presence of even small amounts of thixotropic polymers have a beneficial effect in terms of viscosity reduction under transport conditions.

Suitably, the continuous aqueous phase may comprise

- 5 -

two or more different types of thixotropic hydrophilic polymers.

The invention further provides a process for the preparation of polymer compositions of the invention, which process comprises emulsifying a mixture of polymer A, the surfactant and polymer B at a temperature above the melting point of the polymer A, and cooling the resulting emulsion to a temperature below the melting temperature of polymer A.

The upper temperature limit for the process will be determined by the lowest decomposition temperature of the various components of the mixture. Using acrylate polymers as polymer A, alcohol ethoxy sulphate surfactants and/or lignosulphonate surfactants, and temperatures for emulsifying mixtures in the range 50°C to 100°C has been found to be very effective, temperatures in the range 60 to 100°C being preferred.

Further in accordance with the invention there is provided the use of a composition of the invention in depressing the pour point of a crude mineral oil or a wax-containing fuel oil or diesel oil.

The polymer compositions of the invention have particularly useful application according to the invention in inhibition and/or reduction of wax deposition in crude oil pipelines. The fact that the present aqueous compositions are fluid at lower temperatures than simple solutions of the relevant polymer at corresponding concentrations in solvents such as toluene or xylene confers significant improvements in handleability in lower temperature environments. Moreover, since the present aqueous formulations contain little or none of such solvents they constitute very attractive materials from the safety standpoint (flashpoint), when compared with conventional formulations.

The invention will be further understood from the

- 6 -

following illustrative Examples, in which:-

Polymer I is an alkyl acrylate polymer, mp 51°C, of molecular weight (Mn) in the range 49,000 to 76,000 measured by gel permeation chromatography (GPC)
5 (polyacrylate scale) prepared from a blend of linear alkyl acrylates comprising 1-docosyl acrylate, 1-octadecyl acrylate and 1-eicosyl acrylate.

"DOBANOL 25-3A/60" (trade mark) ethoxy sulphate is a 60%w solution in aqueous ethanol (2:1 w/w) of
10 ammonium (C₁₂-15 alcohol) ethoxy sulphates containing 3 mol ethylene oxide/mol (density at 20°C 1.04 kg/l).

Examples 1 to 6

Water (44.6 g), "DOBANOL 25 - 3A/60" ethoxy sulphate (5 g) and partly hydrated polyacrylamide (PHAM) (0.4 g) were stirred to give a homogenous solution at ambient temperature (20°C) in a 150 ml beaker. Polymer I (50 g) was added and the bottle was transferred to a thermostatic oil bath at 80°C. The two-phase mixture was emulsified using an "ULTRA TURRAX T25" (trade mark) laboratory emulsifier (1.8 cm dispersing tool, at 24,000 r.p.m.) for 1 minute. The resulting emulsion of Polymer I in the aqueous phase was cooled by removing the bottle from the oil bath and allowing it to cool in air to ambient temperature (20°C), to yield the desired composition as a readily flowable suspension.
25

Additional suspensions (Examples 2 to 6) were prepared in a similar manner to the above suspension, except that in Example 4 Xanthan gum was used instead of PHAM and that hexadecyltrimethylammonium bromide (HDTMAB) was used instead of ethoxysulphate; in comparative Example 5 glycerol was used instead of water and PHAM, the temperature of the thermostatic oil bath was 96°C and the mixture was emulsified for 2 minutes; and in comparative Example 6 glycerol was used instead of PHAM, the temperature of the thermostatic
30
35

- 7 -

oil bath was 101°C and the mixture was gently emulsified for 1 minute, after which water was added. Details of all six suspensions and their preparation are given in Table 1.

5 In each case the suspensions were stable at ambient temperature (20°C) for at least one month. The suspensions were all liquid at least down to 5°C. The suspensions were tested by addition to a Far East crude oil and assessment of the pour point according to ASTM 10 D.97. The pour point of the undoped crude oil was 24°C, for examples 1-3, and 30°C for examples 4-6.

The test results of the suspensions of Examples 1 to 6 are summarised in Table II.

15 Viscosity was measured at 20 °C with a cone and plate system in a Carri-Med "CSL 500" Rheometer.

It will be clear from Table II that the suspensions in accordance with the invention (Examples 1-4) display an attractive pour point activity together with an improved low viscosity when compared with suspensions 20 falling outside the scope of the present invention (Examples 5 and 6).

Table I

Example	pbw water	pbw ethoxysulphate	pbw HDTMAB	pbw PHAM	pbw Xanthan gum	pbw glycerol
1	89.6	10	-	0.4	-	-
2	89.8	10	-	0.2	-	-
3	89.2	10	-	0.8	-	-
4	93.4	-	4	-	1.6	-
5	-	4	-	-	-	96
6	15	4	-	-	-	46

pbw = parts by weight/100 parts polymer I

- 9 -

Table II

Example	Viscosity at 20°C (Pa.s)	Rate of addition of suspension to Far East crude oil (kg polymer 1/kg oil)	pour point of treated oil (°C)
1	0.17	1000	12
2	0.08	1000	18
3	0.60	1000	12
4	0.16	925	9
5	13.7	2160	15
6	1.9	2470	12

- 10 -

CLAIMS

1. A polymer composition comprising a dispersion of at least one polymer A obtained by polymerisation of at least one olefinically unsaturated compound, which polymer contains aliphatic hydrocarbon side chains of at least 10 carbon atoms, in a continuous aqueous phase comprising a surfactant and at least one polymer B which comprises a thixotropic hydrophilic polymer.
- 5 2. A composition according to Claim 1 wherein the at least one polymer B is a polysaccharide or a partly hydrated polyacrylamide.
- 10 3. A composition according to Claim 1 or 2 wherein polymer A has a molecular weight (M_n) in the range 20,000 to 250,000.
- 15 4. A composition according to Claim 1, 2 or 3 which contains 0.1 to 20 parts by weight of surfactant per 100 parts by weight of polymer A.
5. A composition according to any one of Claims 1 to 4 which contains 0.01 to 20 parts by weight of polymer B per 100 parts by weight of polymer A.
- 20 6. A composition according to any one of Claims 1 to 5 which contains more than 20 parts by weight of water per 100 parts by weight of polymer A.
7. A composition according to any one of Claims 1 to 6 wherein polymer A is a polymer of one or more (C_{18-26} n-alkyl) acrylates or a copolymer of one or more (C_{18-26} n-alkyl) acrylates and 4-vinyl pyridine.
- 25 8. A composition according to any one of Claims 1 to 7 wherein the surfactant is an alcohol ethoxy sulphate surfactant or a lignosulphonate surfactant.
- 30 9. A process for the preparation of a composition according to any one of Claims 1 to 8 which comprises emulsifying a mixture of polymer A, the surfactant and

- 11 -

polymer B at a temperature above the melting point of polymer A, and cooling the resulting emulsion to a temperature below the melting temperature of polymer A.

10. Use of a composition according to any one of Claims 1 to 8 in depressing the pour point of a crude mineral oil or a wax-containing fuel oil or diesel oil.

5

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 97/02705

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08J3/05 C08J3/03 C08L33/06 C08L39/08 C10L1/10

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08J C08L C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 659 771 A (CRAIG) 21 April 1987 see the whole document ---	1,2,4-8
X	US 4 068 676 A (THORN ET AL.) 17 January 1978 see the whole document ---	1,2,4-7
X	EP 0 290 772 A (HERCULES) 17 November 1988 see the whole document ---	1,2,4-8
X	EP 0 671 435 A (HÜLS) 13 September 1995 see page 2 - page 3 ---	1-7
A	EP 0 448 166 A (SHELL) 25 September 1991 cited in the application see the whole document ---	1-10 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search Date of mailing of the international search report

28 January 1998

09/02/1998

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

De La Morinerie, B

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 97/02705

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 110 283 A (CAPELLE) 29 August 1978 see the whole document -----	1-10
A	DE 42 24 044 A (BOSTIK) 27 January 1994 see the whole document -----	1-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 97/02705

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4659771 A	21-04-87	AU 598475 B-- AU 6170286 A CA 1286828 A EP 0213895 A JP 62070410 A	28-06-90 26-02-87 23-07-91 11-03-87 31-03-87
US 4068676 A	17-01-78	NONE	
EP 290772 A	17-11-88	US 4801643 A AU 604864 B AU 1382688 A CA 1324455 A DE 3885792 D DE 3885792 T JP 63264604 A	31-01-89 03-01-91 29-09-88 16-11-93 05-01-94 24-03-94 01-11-88
EP 671435 A	13-09-95	DE 4407841 A US 5703156 A	14-09-95 30-12-97
EP 448166 A	25-09-91	AU 639539 B AU 7362591 A CA 2038634 A DE 69113496 D DE 69113496 T EG 19136 A ES 2078425 T HK 64297 A JP 4222849 A	29-07-93 14-11-91 22-09-91 09-11-95 07-03-96 30-08-94 16-12-95 23-05-97 12-08-92
US 4110283 A	29-08-78	NONE	
DE 4224044 A	27-01-94	WO 9402556 A	03-02-94